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Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds

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[1] Recent experimental evidence indicates that heterogeneous chemical reactions play an important role in the gas-particle partitioning of organic compounds, contributing to the formation and growth of secondary organic aerosol in the atmosphere. Here we present laboratory chamber studies of the reactive uptake of simple carbonyl species (formaldehyde, octanal, *trans*,*trans*-2,4-hexadienal, glyoxal, methylglyoxal, 2,3-butanedione, 2,4-pentanedione, glutaraldehyde, and hydroxyacetone) onto inorganic aerosol. Gas-phase organic compounds and aqueous seed particles (ammonium sulfate or mixed ammonium sulfate/sulfuric acid) are introduced into the chamber, and particle growth and composition are monitored using a differential mobility analyzer and an Aerodyne Aerosol Mass Spectrometer. No growth is observed for most carbonyls studied, even at high concentrations (500 ppb to 5 ppm), in contrast with the results from previous studies. The single exception is glyoxal (CHOCHO), which partitions into the aqueous aerosol much more efficiently than its Henry's law constant would predict. No major enhancement in particle growth is observed for the acidic seed, suggesting that the large glyoxal uptake is not a result of particle acidity but rather of ionic strength of the seed. This increased partitioning into the particle phase still cannot explain the high levels of glyoxal measured in ambient aerosol, indicating that additional (possibly irreversible) pathways of glyoxal uptake may be important in the atmosphere.

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1. Introduction

[2] Organic compounds are a significant component of total particulate matter (PM) in the troposphere, so the characterization of sources and composition of organic aerosols is important to our understanding of the potential climate forcing and human health effects of atmospheric PM. In particular, secondary organic aerosols (SOA), formed by the condensation of gas-phase oxidation products of volatile organic compounds (VOCs), constitute a substantial fraction of total organic PM, yet details of SOA formation and evolution remain poorly constrained. Understanding such processes poses a number of experimental and theoretical challenges, because of the large number of condensable products in SOA, the structural complexity of such components, and the importance of short-lived and/or highly nonvolatile intermediates in aerosol formation. Nonetheless, absorptive models of gas-particle partitioning [e.g., *Pankow*, 1994a, 1994b; *Odum et al.*, 1996] have generally been successful in describing the total aerosol growth observed in laboratory studies of SOA formation. Such models describe particle growth not in terms of all condensable reaction products but rather in terms of a small number of model semi-volatile products. Aerosol growth may then be described by such products' stoichiometric yields and absorptive gas-particle partitioning constants.

[3] However, recent experimental work indicates that in addition to physical absorption, gas-to-particle partitioning also occurs via particle-phase chemical reactions. High-molecular-weight compounds have been observed in laboratory studies of SOA formation from the ozonolysis of large alkenes [*Tobias and Ziemann*, 2001; *Ziemann*, 2002; *Tolocka et al.*, 2004; *Iinuma et al.*, 2004; *Gao et al.*, 2004a, 2004b; *Bahreini et al.*, 2005] and the photooxidation

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of aromatic compounds [*Kalberer et al.*, 2004]. Such products have masses significantly greater than those of their VOC precursors, indicating the formation of oligomers of VOC oxidation products in the aerosol phase. These additional particle-phase reactions are expected to have a significant influence on gas-particle partitioning, resulting in greater SOA mass than would be expected from the vapor pressures of the VOC oxidation products alone. In addition, total SOA growth is found, in some cases, to be dependent on the chemical composition of the inorganic seed aerosol used, with enhanced aerosol growth when the seed is acidic [*Jang et al.*, 2002; *Czoschke et al.*, 2003; *Iinuma et al.*, 2004; *Gao et al.*, 2004a, 2004b]; since seed composition does not affect the gas-phase chemistry, these results indicate the importance of heterogeneous chemistry in gas-to-particle conversion. Such increases in aerosol growth by reactive uptake may still be described within the context of gas-particle partitioning models, by inclusion of heterogeneous reactions into gas-particle partitioning coefficients [*Kroll and Seinfeld*, 2005].

[4] In order to separate the complex gas-phase chemistry of VOC oxidation from gas-particle partitioning, recent experimental studies have also investigated the SOA-forming potential of individual compounds (or analogs thereof) produced by VOC oxidation. Jang and coworkers [*Jang and Kamens*, 2001a; *Jang et al.*, 2002, 2003a, 2003b, 2005] observed significant aerosol growth when inorganic seed is exposed to a wide variety of organic species; compounds studied include simple C_4–C_{10} aldehydes, unsaturated carbonyl compounds, and dicarbonyl compounds. Growth was generally observed to be greater when the seed acidity was increased. The authors suggested that these carbonyls may undergo acid-catalyzed oligomerization reactions, including hemiacetal (or acetal) formation and aldol condensation. Subsequent theoretical calculations, however, indicated that for many of the compounds studied, such reactions may not be thermodynamically favorable [*Barsanti and Pankow*, 2004].

[5] Reactions of a number of simple (C_1–C_3) gas-phase carbonyls in concentrated sulfuric acid solutions have also been studied, largely to understand the importance of such reactions in the upper troposphere and lower stratosphere. While reactive uptake has been observed for formaldehyde [*Tolbert et al.*, 1993; *Jayne et al.*, 1996; *Iraci and Tolbert*, 1997], acetaldehyde [*Michelsen et al.*, 2004], and acetone [*Duncan et al.*, 1998, 1999; *Klassen et al.*, 1999; *Kane et al.*, 1999; *Imamura and Akiyoshi*, 2000], and even the larger aldehydes octanal and 2,4-hexadienal [*Zhao et al.*, 2005], reactions were generally carried out under highly acidic conditions (>50 wt% H_2SO_4) and at subambient temperatures, conditions not generally relevant for SOA formation in the troposphere. B. Nozière and coworkers found that 2,4-pentanedione may oligomerize via the aldol condensation under tropospheric conditions (297 K, 20 wt% H_2SO_4) [*Nozière and Riemer*, 2003], but also that under such conditions, aldol condensation reactions are too slow to contribute significantly to SOA growth [*Esteve and Nozière*, 2005].

[6] Very recently, *Liggio et al.* [2005a, 2005b] studied aerosol growth by heterogeneous reaction of gas-phase glyoxal (CHOCHO), using aerosol mass spectrometry to observe aerosol growth by oligomer formation. Glyoxal, one of the compounds observed to contribute to aerosol growth by *Jang and Kamens* [2001a] and *Jang et al.* [2002], is formed in a number of VOC oxidation processes, such as the photooxidation of aromatic compounds [*Volkamer et al.*, 2001; *Calvert et al.*, 2002], the ozonolysis of alkenes [*Calvert et al.*, 2000], and the OH + acetylene reaction [*Hatakeyama et al.*, 1986; *Yeung et al.*, 2005], and has recently been used as a tracer for VOC oxidation in urban areas [*Volkamer et al.*, 2005]. The boiling point of glyoxal is 51°C, suggesting it is far too volatile to be physically absorbed into an organic aerosol phase to any appreciable extent. However, *Liggio et al.* [2005a] observed organics in the particle phase of mass greater than that of monomeric glyoxal, strongly suggesting the importance of reactive uptake of glyoxal, which leads to the formation of oligomers (as well as organic sulfates) in the aerosol phase. Rate of glyoxal uptake was also measured [*Liggio et al.*, 2005b], and was found to be somewhat higher when seed particles were acidic. Heterogeneous reaction of a similar compound, methylglyoxal, has also been suggested as a pathway for oligomer formation in SOA from the photooxidation of aromatic compounds [*Kalberer et al.*, 2004]. Evidence for this was based on comparison of mass spectra of aerosol samples with those from bulk-phase methylglyoxal solutions, so reactive uptake of methylglyoxal leading to SOA growth has not yet been explicitly examined.

[7] There thus exists clear and compelling evidence that heterogeneous reactions play an important role in the formation of secondary organic aerosol, via the increase in partitioning of gas-phase organics into the aerosol phase. The formation of oligomeric products may also be important in that it might influence the CCN activation ability [*VanReken et al.*, 2005] or optical properties [*Nozière and Riemer*, 2003] of the aerosol. However, the detailed chemistry, and even the basic mechanism, of such reactions remain poorly understood. The overall, quantitative effect of heterogeneous chemistry on the gas-particle partitioning of organics in the atmosphere is largely unknown, especially since it is likely to be dependent on a large number of factors, including temperature, relative humidity, particle size, and particle composition. Understanding such effects is necessary for the interpretation of mechanisms of aerosol growth as measured in the laboratory, as well as for the accurate modeling of SOA formation and evolution in the atmosphere.

[8] In particular, the role of seed acidity in SOA growth remains poorly constrained. While an increased rate of aerosol-phase chemical reactions (acid catalysis) may explain observed increases in uptake coefficients, it does not explain observed increases in total (equilibrium) aerosol yields in the presence of acidic seed [*Czoschke et al.*, 2003; *Iinuma et al.*, 2004; *Gao et al.*, 2004a, 2004b; *Jang et al.*, 2005]. Henry's law coefficients of many carbonyls are known to increase dramatically at high acidities [e.g., *Kane et al.*, 1999; *Nozière and Riemer*, 2003; *Michelsen et al.*, 2004], but it is not clear whether this is also the case for the absorptive gas-particle partitioning coefficients which govern SOA formation. While reactions that occur within acidic

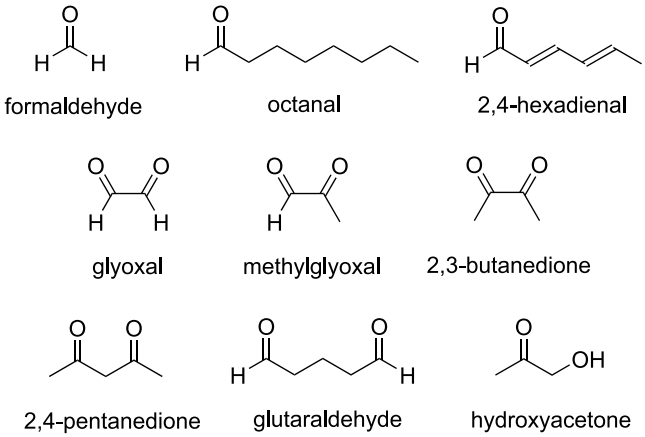

Figure 1. Structures of the carbonyls studied in this work.

particles may not be accessible under milder conditions, such differences in chemistry have not been conclusively identified; formation of oligomers has been observed even in the absence of inorganic seed [*Kalberer et al.*, 2004; *Gao et al.*, 2004a, 2004b]. Few studies of ambient aerosols have examined the relationship between acidity and organic content of aerosols, though recent measurements made in Pittsburgh reveal no significant enhancement of the organic fraction in acidic particles [*Zhang et al.*, 2005]. Therefore both the chemical mechanism and the atmospheric significance of increased uptake of organics by acidic particles are at present poorly understood.

[9] The role of reactive uptake by small, volatile carbonyls (such as glyoxal [*Liggio et al.*, 2005a, 2005b], methylglyoxal [*Kalberer et al.*, 2004], and short-chain aldehydes [*Jang and Kamens*, 2001a]) in SOA formation is also not well established. If such chemistry results in significant particle growth, then SOA may be formed by a much wider range of VOC oxidation processes than is currently believed, and the oxidation of simple, short-chain hydrocarbons may even contribute to global SOA. It is therefore especially important to understand whether heterogeneous reactions lead to the partitioning of these smaller carbonyls into the particle phase.

[10] In this study, we examine the potential for SOA growth via heterogeneous reactions for a number of such compounds (shown in Figure 1), by measuring changes in particle volume and composition when inorganic seed and gas-phase carbonyls are introduced into an environmental chamber. We observe no significant growth for most compounds studied, in contrast with the results from previous studies. We do, however, observe substantial growth by gas-phase glyoxal, consistent with the results of *Liggio et al.* [2005a]. Whereas the work of Liggio et al. investigated the mechanism and kinetics of the oligomerization reactions [*Liggio et al.*, 2005a] and rate of reactive uptake [*Liggio et al.*, 2005b], here we focus on the equilibrium partitioning of glyoxal between the gas and particle phases. Total (equilibrium) aerosol growth is measured as a function of glyoxal concentration, initial inorganic seed volume, and seed acidity, and from these data a gas-particle partitioning coefficient is determined. This coefficient is then compared to ambient measurements of glyoxal in the gas and particle phases, as a test of our understanding of atmospheric gas-particle partitioning.

2. Experiment

[11] Experiments are carried out in the Caltech Indoor Chamber Facility; instrumentation and methods have been described in detail elsewhere [*Cocker et al.*, 2001; *Keywood et al.*, 2004], so will be described only briefly here. The facility consists of two indoor 28 m^3 Teflon (PFE) chambers, designed for the minimization of wall loss and for the control of temperature, relative humidity, and photolytic conditions. For experiments described here, temperature is held at 20 (±1) °C; relative humidity (RH) is controlled by sending clean air through large bubblers prior to introduction into the chamber. Temperature and RH are continually monitored. For a few initial experiments (particle growth by uptake of simple carbonyls), studies were carried out in a smaller, 3 m^3 chamber; for these studies, experimental protocols and instruments used are the same as used in the larger chambers. All experiments were carried out under dark conditions, to avoid unwanted photolysis of reactants and products.

[12] Particle volume is continually monitored by a differential mobility analyzer (DMA, TSI 3081) coupled to a condensation particle counter (CPC, TSI 3760), with settings identical to those described by *Keywood et al.* [2004]. All aerosol volume data are corrected for wall loss; standard correction techniques (application of the number concentration decay constant to total particle volume) cannot be used, as the implicit assumption that size distribution remains constant introduces errors that are too large for the small growths measured here. Instead, size-dependent decay coefficients are determined from "wall-loss" experiments, in which the exponential loss of seed aerosol under clean (organic-free) conditions is measured. Application of these decay coefficients leads to an overcorrection, due to deviations from the exponential fit, as well as the effect of coagulation, which leads to changes in number concentration but not in total particle volume. This overcorrection, empirically determined to be ~9 $\mu m^3/cm^3$, is subtracted from all measurements of particle growth presented here. This subtraction is valid as long as the time-dependent size distributions in particle growth experiments are similar to those in the "wall-loss" experiments. This is the case for the present experiments, as organic growth is small relative to the initial seed volume. As an additional check of total aerosol number concentration, particle number is monitored in each chamber by separate CPCs (TSI 3010 and 3025).

[13] For most experiments, particle composition and mass are monitored using an Aerodyne Aerosol Mass Spectrometer (AMS). Operation and calibration of this instrument have been described elsewhere [*Jayne et al.*, 2000; *Allan et al.*, 2003, 2004; *Bahreini et al.*, 2005] and will not be discussed here. The AMS allows for the quantitative measurement of inorganic (ammonium and sulfate) and organic mass within the aerosol. Organic species undergo decomposition in the vaporizer (~600°C) and fragmentation during electron impact ionization (70 eV) so cannot be identified individually. Nonetheless, it has been shown that fragmentation patterns of organic aerosols may be useful for

understanding details of particle-phase oligomerization reactions [*Liggio et al.*, 2005a; *Bahreini et al.*, 2005].

[14] For most carbonyl + seed experiments (with the exception of glyoxal; see below), the inorganic seed is introduced into the chamber prior to introduction of the organic. Polydispersed seed particles are generated by atomization (at 30 psi) of dilute salt solutions; in all experiments described here the seed used is either ammonium sulfate (0.03M) or mixed ammonium sulfate/sulfuric acid (0.03M/0.1M).

[15] Structures of the organic compounds studied in this work are shown in Figure 1. Most are introduced into the gas phase by sending air over a measured volume of the pure compound and into the chamber, though the less volatile compounds (boiling point >120°C) require gentle heating for efficient evaporation. Care is taken to keep this heating to a minimum, as overheating was found to lead to new particle formation, presumably because of supersaturation of the gas-phase organic in the injection line; this causes a significant increase in particle number and sometimes particle volume. Compounds used are all from Aldrich and are: octanal (99%), *trans-trans*-2,4-hexandienal (95%), 2,3-butanedione (97%), 2,4-pentanedione (99+%), glutaraldehyde (25% in water), and hydroxyacetone (≥90%). Concentrations of these compounds are estimated by volume of hydrocarbon injected, and monitored with gas chromatography with flame ionization detection (GC-FID). For initial tests of whether these compounds contribute to aerosol growth, high concentrations (500 ppb to 5 ppm) are used, and no calibrations of GC-FID response were made.

[16] The three smallest compounds shown in Figure 1, formaldehyde, glyoxal, and methylglyoxal, could not be introduced efficiently into the gas phase by the above method, nor could they be detected with simple GC-FID. Instead, gas-phase monomers are prepared from the commercially available polymeric (formaldehyde and glyoxal) or aqueous (glyoxal and methylglyoxal) forms. The aqueous compounds are dried down first: aqueous glyoxal or methylglyoxal (both 40 wt%, Aldrich) is evaporated under vacuum until it becomes a white crystalline solid (glyoxal) or viscous yellow liquid (methylglyoxal). After addition of P_2O_5, the dried compound is gently heated under vacuum until it starts bubbling, indicating the release of gas-phase monomer. The monomer passes through an LN_2 trap, where it is collected as a solid. The same procedure, minus the initial drying step, is used to prepare formaldehyde from the solid paraformaldehyde (Aldrich, ≥95%) or glyoxal from solid trimeric glyoxal dihydrate (Aldrich, ≥97%). To obtain a fixed amount of gaseous compound, the LN_2 is removed, allowing the frozen monomer to slowly vaporize into a 500 mL glass bulb to a desired pressure, as measured with a capacitance manometer (MKS); care is taken to allow any CO_2 collected in the trap to escape first. FTIR measurements of the collected gas-phase glyoxal confirm that the glyoxal is pure, with minimal CO and CO_2 impurities, and is present only in monomeric form: its spectrum matches that published previously [*Niki et al.*, 1985], and has no observable C-O or O-H features, which would suggest polymerization and/or hydration. Further, both FTIR and bulb pressure measurements indicate that, under dry conditions, glyoxal is not lost in significant amounts to glass surfaces. Under humid conditions, however, rapid loss of gas-phase glyoxal is observed, as is the formation of polymers on the walls of the vessel. Finally, the glass bulb is attached to the chamber and a stream of dry air is passed through the bulb, introducing the carbonyl into the chamber.

[17] Formaldehyde, glyoxal, and methylglyoxal are measured by solid-phase microextraction (SPME) with on-fiber derivatization, using *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA, Aldrich, 98+%) [*Martos and Pawliszyn*, 1998; *Reisen et al.*, 2003]. The SPME sampler used in this study is a 65 μm poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) fiber mounted in a portable syringe holder (Supelco). After conditioning at 250°C for at least half an hour, the fiber is coated with PFBHA by exposing it to the headspace of aqueous PFBHA (17 mg/mL) for 30 min. The coated fiber is then exposed to the chamber through a septum for 15 min. Introduction of the fiber into the GC injection port at 250°C desorbs the resulting oximes (formed by the reaction of PFBHA + aldehyde) onto the column, through which they readily elute, allowing for detection by FID. For each experiment, 3–4 SPME measurements are made per chamber; values obtained generally agree to within 10–15%.

[18] While this technique allows for the detection of formaldehyde, glyoxal, and methylglyoxal, we calibrate it only for glyoxal, the focus of this work (concentrations of the other compounds are estimated by pressure in the glass collection bulb). To calibrate, 5.2 Torr of gas-phase glyoxal is introduced into a 2 L glass bulb, which is brought to atmospheric pressure by addition of nitrogen. A fixed volume (0.5–2.0 mL) of the gas-phase sample is removed using an airtight syringe, and added to a sealed Teflon bag containing 40 L of dry air. The resulting glyoxal concentrations (85–340 ppb) are used as calibration standards. FID signal is linear with glyoxal at these concentrations; any losses of glyoxal to surfaces (in the collection bulb, syringe, or Teflon bag) during calibration will affect the accuracy but not the precision of the measurements. We are unable to perform calibrations at higher relative humidity, because of the loss of glyoxal on surfaces at high RH (see below); however, changes in RH are not expected to affect the SPME calibration significantly [*Reisen et al.*, 2005].

[19] At values of RH above 30%, and especially at higher humidity, rapid loss of glyoxal, presumably uptake to the chamber walls, is observed: upon introduction of 500 ppb glyoxal into the 28 m^3 chamber at 51% RH, approximately half is depleted after 6 hours. After several more hours the concentration eventually stabilizes, reaching equilibrium between glyoxal on the walls and in the gas phase. Equilibrium concentrations can be as high as 200 ppb, significantly higher than the 3.6–5.4 ppb concentration observed by *Liggio et al.* [2005a]; the reason for this discrepancy is not clear. To ensure constant levels of gas-phase glyoxal over the course of an experiment, the inorganic seed is introduced only after the glyoxal concentrations are observed to stabilize. As noted by *Liggio et al.* [2005a], glyoxal tends to be persistent on Teflon surfaces, so flushing the chamber for a few hours after the experiment is not sufficient to remove all glyoxal from the system. By flushing the chambers for ~36 hours between experiments, enough glyoxal has been removed so that its equilibrium gas-phase concentration is measurably lower, and an experiment at the new concentration may be performed. Thus a

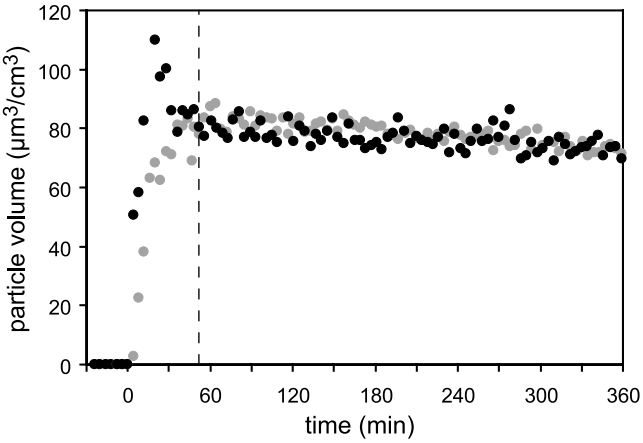

Figure 2. Sample DMA volume data for chamber experiments. Introduction of inorganic seed corresponds to $t = 0$; the gradual decrease in volume is a result of particle loss to the chamber walls. Grey circles, inorganic seed only. Black circles, inorganic seed (ammonium sulfate/sulfuric acid), followed by introduction of 500 ppb 2,4-hexadienal at $t = 50$ min (dashed line). Data are scaled so that starting particle volumes are equivalent.

number of measurements may be made over the few days following a single glyoxal injection.

3. Results and Discussion

3.1. Uptake of Organics: Carbonyl Compounds Other Than Glyoxal

[20] For all the carbonyl compounds studied (Figure 1), with the exception of glyoxal, we observe no aerosol growth, in either the DMA or the AMS. In some experiments carried out overnight, DMA particle volume is observed to level out somewhat (or in one case, to increase slightly) for a period of a couple hours; the resulting calculated growth after correction for wall loss is small (0–5 $\mu m^3/cm^3$). However, in these instances no organic growth is observed in the AMS (detection limit of $\sim$0.5 $\mu g/m^3$, with 2 min averaging), and the period of leveling off coincides with a decrease in temperature (and therefore an increase in RH), presumably arising from temperature changes outside and/or poor thermostatting of the room. Therefore the small growth observed is from water uptake by the inorganic seed rather than uptake of the organic compound. Such fluctuations were not observed for the glyoxal experiments.

[21] Shown in Figure 2 are the raw DMA particle volume data (not corrected for wall loss) from a typical experiment, 500 ppb of 2,4-hexadienal in the presence of acidic seed (54–56% RH). Also shown is a "seed-only experiment," in which seed but no organic is introduced. Both experiments were carried out in the same 28 m^3 chamber, and data are scaled to the same initial seed volume. No substantial difference in particle volume is observed between runs with and without 2,4-hexadienal. Similarly, introduction of $\sim$960 ppb methylglyoxal, which has been implicated in oligomer formation during photooxidation of aromatic compounds [*Kalberer et al.*, 2004], results in negligible growth: volume measured by the DMA, after correction for wall loss, shows a small (<5 $\mu m^3/cm^3$) volume increase, but no organic growth is observed by the AMS. Similar results are obtained for the other carbonyls studied (save glyoxal): no growth is observed for formaldehyde (5 ppm), octanal (500 ppb), 2,3-butanedione (500 ppb), glutaraldehyde (500 ppb), 2,4-pentanedione (5 ppm), and hydroxyacetone (3 ppm), all at 50–55% RH.

[22] The lack of growth at these high concentrations, when scaled to tropospheric carbonyl concentrations, suggests that reactive uptake of these species onto inorganic aerosols is not significant in the troposphere. These results are in stark contrast to those of Jang and coworkers [*Jang and Kamens*, 2001a; *Jang et al.*, 2002, 2003a, 2003b, 2005], who report significant aerosol growth for a number of carbonyl compounds. While it is difficult to compare the present chamber data with their flow reactor measurements [*Jang et al.*, 2003a, 2003b], which involve shorter experimental timescales and much higher carbonyl concentrations, their chamber experiments Jang and coworkers [*Jang and Kamens*, 2001a; *Jang et al.*, 2003a, 2005] may be directly compared to ours, as both are carried out with ammonium sulfate or mixed ammonium sulfate/sulfuric acid seed and gas-phase carbonyl concentrations of hundreds to thousands of parts per billion. Using octanal as an example, we observe no growth at 500 ppb, whereas *Jang and Kamens* [2001a] find that concentrations of 1.3 ppm lead to particle growths of 125–329 $\mu m^3/cm^3$ and *Jang et al.* [2005] find that 230 ppb octanal leads to 44–137 $\mu m^3/cm^3$ growth. Similar differences arise for 2,4-hexadienal: we observe no growth at 500 ppb, while *Jang et al.* [2003a] measure 118 $\mu m^3/cm^3$ growth at 3.4 ppm and *Jang et al.* [2005] measure 15–65 $\mu m^3/cm^3$ growth at 328 ppb. Hence even at lower carbonyl concentrations than are used in this study they measure significant aerosol growth. They observe particle growth to be immediate (occurring within 3 min of introduction of the carbonyl), and, in some instances at least, accompanied by an increase in particle number concentration [*Jang and Kamens*, 2001a], which is inconsistent with heterogeneous reaction. Further research is needed to understand the source of this discrepancy.

3.2. Uptake of Organics: Glyoxal

[23] By contrast, using both the DMA and AMS we observe significant particle growth with glyoxal in the presence of aqueous seed, consistent with the results of *Liggio et al.* [2005a]. Shown in Figure 3 are aerosol volume data (before wall-loss correction) for an experiment in which first acidic seed and then 200 ppb glyoxal are added to the chamber at 48% RH. This figure is for illustrative purposes only; since glyoxal is rapidly lost to the walls, the integrated glyoxal concentration may be lower than 200 ppb. As discussed in the Experimental section, for quantitative measurements of particle growth, glyoxal is added first and seed is added only after the glyoxal concentration has stabilized. In all experiments, particle volume is observed to level out after a few hours, though gas-phase glyoxal concentrations remain high.

[24] Aerosol mass spectra of the organic fraction of the aerosols are in agreement with those measured by *Liggio et al.* [2005a] and so are not discussed here. Ion fragments of masses greater than m/z = 58 (the molecular weight of glyoxal) indicate the presence of hydrates and oligomers of

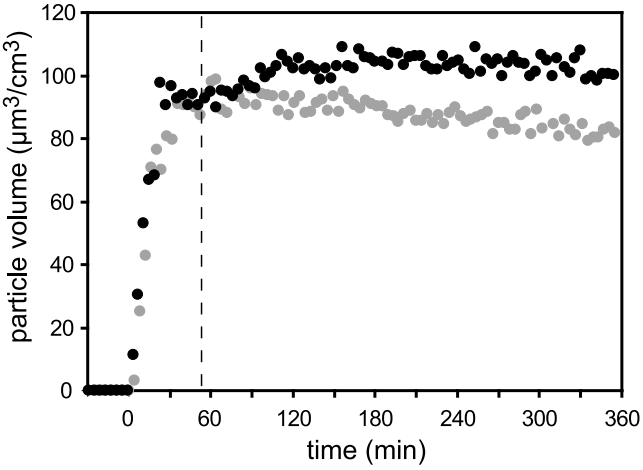

Figure 3. DMA volume data growth for a glyoxal + inorganic seed experiment. As in Figure 2, introduction of inorganic seed corresponds to $t = 0$. Grey circles, inorganic seed only. Black circles, inorganic seed (ammonium sulfate/sulfuric acid), followed by introduction of 200 ppb glyoxal at $t = 53$ min (dashed line). Data are scaled so that starting particle volumes are equivalent.

glyoxal, and observed masses and relative intensities match those measured by *Liggio et al.* [2005a] well.

[25] Table 1 summarizes experimental conditions and aerosol growth (ΔM) for all glyoxal experiments carried out for glyoxal concentrations $\leq$200 ppb. Total aerosol volume is measured by the DMA and converted to mass by assuming unit density. Uncertainties in ΔM arise from signal-to-noise of the DMA volume measurement ($\sigma \approx 2.0$ $\mu m^3/cm^3$) and do not include uncertainties inherent in the wall-loss correction, which are difficult to quantify. Water content of the seed aerosol is estimated using molalities of aqueous solutions at the experimental RH, as obtained from the ISORROPIA aerosol thermodynamic equilibrium model database [*Nenes et al.*, 1998]; for the mixed ammonium sulfate/sulfuric acid seed, water content of the individual components is assumed to add linearly, on the basis of the relative ratios (0.3:1.0) in the seed solution.

[26] Aerosol growth is observed for all experiments shown in Table 1. Considerably larger growth is observed at even higher glyoxal concentrations. Glyoxal uptake may be accompanied by loss of water in the seed, or may occur as the seed particles are still mixing (first 30 min of the experiment); such effects would lead to an underestimate of organic growth. Comparison of organic mass measured by the AMS with particle volume measured by the DMA suggests these are relatively minor effects, and any errors introduced are proportional to total growth. Only a small fraction of the aerosol volume (at the start and end of the experiment) is from particles larger than the DMA cutoff ($\sim$820 nm); neglect of such large particles therefore has minimal effect on measured aerosol growth.

[27] Tests in the 3 m^3 chamber using dry ammonium sulfate seed (12% RH) show zero growth, even at glyoxal concentrations as high as $\sim$1 ppm, consistent with the results of *Liggio et al.* [2005a]. This strongly suggests that glyoxal first partitions into the aerosol phase by dissolution into the aqueous seed, so a Henry's law treatment of glyoxal uptake is appropriate:

$$\Delta M = [\mathrm{Gly_A}] = 10^{-12} K_H^*(mw) V [\mathrm{Gly_G}] \quad (1)$$

in which ΔM is change in aerosol mass, $[\mathrm{Gly_A}]$ is the mass concentration of glyoxal in the aerosol phase ($\mu g/m^3$), $[\mathrm{Gly_G}]$ is the glyoxal concentration in the gas phase (ppb), K_H^* is the effective Henry's law constant of glyoxal (M/atm), mw is the molecular weight of glyoxal (g/mol), and V is the volume concentration of aqueous seed ($\mu m^3/cm^3$) (the 10^{-12} is for units conversion). This relation assumes that gas-phase glyoxal concentration $[\mathrm{Gly_G}]$ is constant, and becomes somewhat more complex if gas-phase glyoxal decreases during gas-particle partitioning [*Kroll and Seinfeld*, 2005]; however, no significant decrease is observed.

[28] By equation (1), aerosol growth is expected to be linear with concentration of gas-phase glyoxal ($[\mathrm{Gly_G}]$) as well as the volume of aqueous seed (V). While linear relationships between concentrations of a condensable compound in the gas and particle phases are not typical in SOA formation [*Odum et al.*, 1996], they may occur in systems in which the absorbing medium is inorganic, so that uptake of the organic does not affect the amount of absorbing medium [*Kroll and Seinfeld*, 2005]. Shown in Figure 4 is a plot of aerosol growth ΔM vs. the product of gas-phase glyoxal concentration $[\mathrm{Gly_G}]$ and volume of aqueous seed V. The linearity is clear, with the exception of one large outlier (experiment 7; 174 ppb glyoxal, acidic seed). The data

Table 1. Experimental Conditions and Measured Particle Growth for Glyoxal Uptake Experiments[a]

Experiment	Seed[b]	[Glyoxal], ppb	RH	Seed Volume V, $\mu m^3/cm^3$	Water Content of Seed[c]	ΔM,[d] $\mu g/m^3$
1	AS	55 ± 7	47.5%	65.3 ± 1.5	31%	5.8 ± 2.0
2	AS	153 ± 7	54.5%	86.8 ± 1.8	36%	18.8 ± 2.8
3	AS	126 ± 5	53.5%	86.5 ± 2.6	35%	14.5 ± 3.1
4	AS	110 ± 4	44.5%	68.5 ± 2.1	30%	7.6 ± 2.4
5	AS	158 ± 20	54.5%	91.7 ± 2.2	36%	21.3 ± 3.3
6	AS/SA	25 ± 3	31.0%	77.4 ± 2.0	42%	0.7 ± 2.5
7	AS/SA	174 ± 8	48.5%	115.4 ± 1.9	51%	11.8 ± 2.7
8	AS/SA	93 ± 12	50.0%	97.3 ± 1.7	52%	10.7 ± 2.5
9	AS/SA	60 ± 7	52.5%	97.6 ± 1.9	53%	10.3 ± 3.0

[a]Reported uncertainties of 1σ.
[b]AS, ammonium sulfate (seed solution 0.03M); AS/SA, mixed ammonium sulfate/sulfuric acid seed (seed solution 0.03M/0.1M).
[c]Percent water by mass.
[d]Assuming unit density of the organic aerosol.

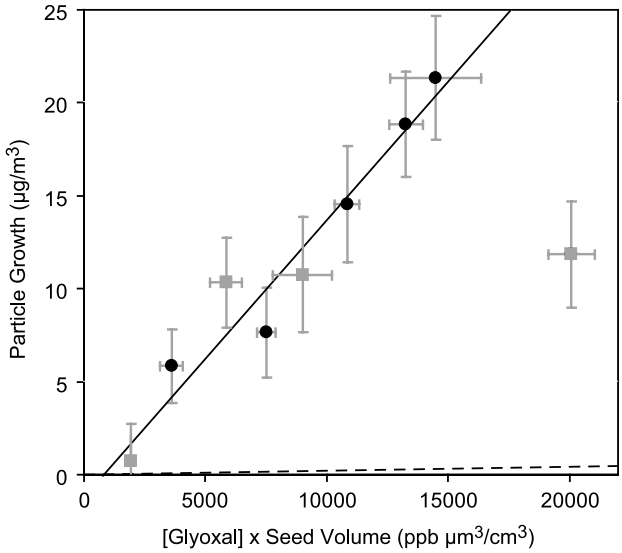

Figure 4. Particle growth as a function of gas-phase glyoxal concentration and initial seed volume, assuming unit density of the organic fraction of the aerosol. Black circles, ammonium sulfate seed. Grey squares, mixed ammonium sulfate/sulfuric acid seed. The fit shown is to the ammonium sulfate data only. The dashed line near the bottom of the figure is the growth expected using the measured Henry's law constant (in seawater) of 3.6×10^5 M/atm [*Zhou and Mopper*, 1990].

collected in that experiment do not seem particularly anomalous, so the source of the large discrepancy is not clear. We therefore first examine only the ammonium sulfate data; the effect of particle acidity will be discussed subsequently.

[29] Linear fitting to the data from the experiments with ammonium sulfate seed (experiments 1–5), yields an effective Henry's law constant of 2.6×10^7 M/atm (the same value is obtained by fitting all data except experiment 7). This value scales linearly with our glyoxal calibration, so any glyoxal losses that may have occurred during calibration (namely surface losses) would lead to an underestimate of the actual value. Moreover, this value depends on the density of the organic fraction of the aerosol, which we assume to be unity; while it is likely to be somewhat greater, it is difficult to estimate. Additionally, the high organic content (up to 20% by volume) may lead to deviations from Henry's law behavior, but the linearity seen in Figure 4 suggests this is not a major effect. Other possible errors in our organic growth measurements (such as those described above) are expected to be proportional to glyoxal uptake, and so do not affect the linearity shown in Figure 4. These potential errors in our calculated effective Henry's law constant are all expected to be relatively small, and do not affect our conclusions substantially.

[30] The dashed line near the bottom of Figure 4 represents the expected amount of aerosol growth based on the measured effective Henry's law constant for glyoxal (in seawater) of 3.6×10^5 M/atm [*Zhou and Mopper*, 1990]. While there are no measurements of the Henry's law constant for glyoxal in pure water (*Betterton and Hoffmann* [1988] determined a lower limit of 3.0×10^5 M/atm), it is unlikely to be significantly different from this value. Comparison of the two lines indicates that glyoxal uptake on ammonium sulfate aerosols is far higher (by a factor of ~70) than glyoxal uptake by water.

[31] The source of this very large increase in partitioning coefficient is not immediately clear. While *Jang and Kamens* [2001a] observed aerosol growth by glyoxal uptake to increase with particle acidity, we do not observe this effect. In fact, measured growth in mixed ammonium sulfate/sulfuric acid seed may be even lower than that in ammonium sulfate seed. Therefore we conclude that increased particle acidity does not promote partitioning of glyoxal into the aerosol phase appreciably. Instead, this partitioning may be controlled by the ionic strength of the seed aerosol ("salting in"). Ammonium sulfate and sulfuric acid are fairly concentrated in the particles (total concentrations of 6.5–7.5 M), leading to high ionic strengths. The higher water content of mixed ammonium sulfate/sulfuric acid seed leads to a somewhat lower (~10–15%) ionic strength than in ammonium sulfate. *Liggio et al.* [2005a] observed significant growth using neutral seeds (sea salt and sodium nitrate), which also suggests that high ionic strength (rather than high acidity) leads to increased uptake. Therefore the factors that control reactive uptake of glyoxal are apparently different than those controlling uptake of condensable species formed in α-pinene ozonolysis, in which growth is higher in the presence of acidic seed [*Czoschke et al.*, 2003; *Iinuma et al.*, 2004; *Gao et al.*, 2004a, 2004b]. The effect of seed composition on gas-particle partitioning may thus be extremely complex. Further research on the effect of the seed particle identity and concentration, including measurements of glyoxal uptake in the bulk phase, may be useful for understanding this effect.

4. Implications

[32] We have shown that reactive uptake of glyoxal on aqueous seed aerosols may lead to significant particle growth, consistent with the results of *Liggio et al.* [2005a]. Results from this study also indicate that reactive uptake of other small, volatile carbonyls (shown in Figure 1) onto inorganic seed is not important under most tropospheric conditions and therefore does not contribute significantly to global SOA production. Most important is the lack of uptake of formaldehyde, the most abundant carbonyl in the troposphere. Further studies are certainly necessary, as results of similar experiments reported by Jang and coworkers [*Jang and Kamens*, 2001a; *Jang et al.*, 2002, 2003a, 2003b, 2005] do not agree with our observations. From our experiments we cannot rule out the possibility that uptake of such simple carbonyls may occur on highly acidic (i.e., ≥50% H_2SO_4) particles. Such high acidities are not common in tropospheric particles but may occur in plumes from coal-burning power plants [e.g., *Brock et al.*, 2002], or by freshly nucleated particles [*Zhang et al.*, 2004]; ambient measurements of the organic fraction of such particles are at present scarce.

[33] We emphasize that the present work focuses only on small, relatively volatile (bp < 200°C) carbonyl compounds. It is expected that reactive uptake by larger carbonyls contribute to SOA; the combination of low volatility and high reactivity may lead to effective gas-particle partitioning

coefficients large enough to lead to significant particle growth. Heterogeneous reactions of such compounds have been implicated in oligomer formation in SOA from α-pinene ozonolysis [*Tolocka et al.*, 2004; *Iinuma et al.*, 2004; *Gao et al.*, 2004a, 2004b]. Additionally, the potential role of cross-reactions, such as the reaction of a low-volatility compound in the particle phase with a more volatile gas-phase carbonyl, has yet to be explored in detail.

[34] In contrast to the other carbonyls studied in this work, glyoxal is found to contribute substantially to aerosol growth. The adjacent electron-poor aldehydic carbons contribute to high water solubility and reactivity of glyoxal, making hydration and oligomerization relatively facile. However, no growth is observed from gas-phase methylglyoxal, presumably because of its more stable (less electron deficient) ketone moiety. From these results the gas-particle partitioning constant for methylglyoxal is at least 30 times lower than that of glyoxal; this is consistent with determinations of effective Henry's law constants for the two compounds, which find methylglyoxal to be 10–100 times less soluble than glyoxal in water [*Betterton and Hoffmann*, 1988; *Zhou and Mopper*, 1990]. Similarly, we observe no particle growth from 2,3-butanedione, an α-diketone with a still lower Henry's law constant [*Snider and Dawson*, 1985; *Betterton*, 1991]. Hence the observed reactive uptake of glyoxal cannot be generalized to all other atmospheric α-dicarbonyls. It seems likely, however, that more highly functionalized carbonyl compounds, such as the polycarbonyls produced in the photooxidation of aromatic compounds [*Yu et al.*, 1997; *Jang and Kamens*, 2001b; *Edney et al.*, 2001] may undergo significant reactive uptake similar to that observed for glyoxal.

[35] Our measurements of the reactive uptake of glyoxal are in qualitative agreement with those by *Liggio et al.* [2005a]. However, it is difficult to compare the results from these two studies directly. In the studies by *Liggio et al.* [2005a], equilibrium had not yet been reached by the end of the experiments (the organic:sulfate ratio continued to increase), perhaps a result of the chamber walls serving as a continual source of gas-phase glyoxal (organic aerosol growth exceeded initial amount of gas-phase glyoxal). Such conditions allow for the study of the kinetics, but not the thermodynamics, of glyoxal uptake. By contrast, the long mixing timescales of the present chamber experiments (there is no active mixing within our chambers) preclude the study of uptake kinetics. However, in these studies gas-particle equilibrium is reached, as particle volume stops increasing after an initial period of growth. Thus these two studies address different characteristics of glyoxal uptake (kinetics and thermodynamics), which likely explains the observed differences in the role of seed acidity in particle growth.

[36] Our observation that particle growth stops even while glyoxal is still present in the gas phase indicates that the reactive uptake of glyoxal is fully reversible. This conclusion is also supported by observations of equilibrium between glyoxal in the gas phase and on chamber walls, both in the present work and in that of *Liggio et al.* [2005a]. Further, in laboratory studies of aqueous glyoxal, equilibrium between gas-phase and aqueous-phase glyoxal has been observed [*Zhou and Mopper*, 1990], as has equilibrium between hydrated glyoxal monomer and dimer (the dominant forms of aqueous glyoxal at concentrations below 10M) [*Whipple*, 1970; *Fratzke and Reilly*, 1986]; such experiments also strongly suggest the reversibility of glyoxal uptake.

[37] By treating glyoxal uptake as reversible, with gas-phase and particle-phase glyoxal in equilibrium, concentrations of particulate glyoxal in the troposphere may be estimated, on the basis of measurements of ambient gas-phase glyoxal in the gas phase, the effective Henry's law constant, and the water content of tropospheric aerosols. This equilibrium approach yields calculated particle-phase glyoxal concentrations that are significantly lower than if glyoxal uptake were assumed to be irreversible. The assumption of irreversibility, in which aerosol growth is determined only by the kinetics of glyoxal uptake, was found to lead to unreasonably high aerosol mass, particularly in urban areas [*Liggio et al.*, 2005b].

[38] Ambient measurements of glyoxal concentrations in urban areas, using sampling and derivatization techniques, indicate that glyoxal levels can be highly variable, ranging from 10 ppt to 1 ppb, with more polluted areas typically having higher levels [*Lee et al.*, 1998; *Kawamura et al.*, 2000; *Jing et al.*, 2001; *Grosjean et al.*, 2002; *Ho and Yu*, 2004]. Recent spectroscopic measurements of ambient glyoxal in Mexico City show significantly higher concentrations, often exceeding 1 ppb in the daytime [*Volkamer et al.*, 2005]. Using our measured effective Henry's law coefficient of 2.6×10^7 M/atm and assuming 100 ppt gas-phase glyoxal and 10 $\mu m^3/cm^3$ of aqueous aerosol (corresponding to 10 $\mu g/m^3$ of ammonium sulfate at 50% RH) in urban air, 1.5 ng/m^3 of glyoxal will be in the particle phase; at the highest measured concentration (1.82 ppb in Mexico City [*Volkamer et al.*, 2005]), particle-phase concentration will be 27 ng/m^3. In rural areas, gas-phase glyoxal concentrations are somewhat lower, varying from 10 to 100 ppt [*Lee et al.*, 1995; *Grossmann et al.*, 2003; *Matsunaga et al.*, 2004], so even lower aerosol-phase glyoxal concentrations are predicted.

[39] There exist few measurements of particulate glyoxal concentrations to which these estimates may be compared, and in only one study [*Matsunaga et al.*, 2004] have both gas- and particle-phase glyoxal concentrations been measured. Such a comparison is also made difficult by the fact that glyoxal oligomers may revert to monomeric form during sampling and derivatization [*Jang and Kamens*, 2001a], and derivatization conditions such as temperature, choice of solvent, and pH may affect the extent of this reversion. Still, measurements of particle-phase glyoxal made in British Columbia, Canada, by *Liggio and McLaren* [2003] are generally in agreement with these predictions, with concentrations of 0.47–1.4 ng/m^3 in Vancouver and 0.43–3.3 ng/m^3 in rural areas. However, comparison with other studies shows poorer agreement: particulate glyoxal concentrations as high as 46 ng/m^3 [*Kawamura*, 1993] and 73 ng/m^3 [*Kawamura and Yasui*, 2005] have been measured in and near Tokyo, and concentrations measured by *Matsunaga et al.* [2004] in Hokkaido Island, Japan (a rural site), averaged 32 ng/m^3 (and were as high as 154 ng/m^3). In that study, glyoxal was found to partition roughly equivalently between the gas and particle

phases, suggesting a gas-particle partitioning coefficient orders of magnitude higher than what we determine.

[40] Hence, while ambient measurements are scarce, it appears that in some cases more glyoxal partitions into the particle phase than would be expected from the results of this study. Particulate glyoxal has even been measured in polar regions, in which gas-phase glyoxal concentrations are expected to be close to zero [*Kawamura et al.*, 1996]. One possible explanation for such discrepancies is the incorporation of glyoxal (as well as methylglyoxal, etc.) into the aerosol phase via heterogeneous reactions with other, less volatile organic compounds already in the aerosol phase. Complexation of glyoxal with inorganic aerosol components (such as metals) may also contribute. Alternately, rapid evaporation of liquid water within aerosols (or cloud droplets) may drive dissolved glyoxal toward higher-order oligomers. Any of these particle-phase processes may be effectively irreversible under tropospheric conditions, and if glyoxal reverts back to its monomer form during sample preparation and/or derivatization, this may lead to measured particulate glyoxal concentrations that are higher than predicted. Further laboratory studies using a wide range of reaction conditions (in particular, using different seed particle compositions) are necessary to understand the importance of such processes.

[41] Moreover, this work underscores the need for ambient measurements of individual compounds in both the gas and particle phases simultaneously. Comparison of partitioning coefficients measured in the atmosphere with those measured in the laboratory provides a powerful test of our understanding of gas-particle partitioning processes in the atmosphere, and in particular our understanding of the role of heterogeneous chemistry in SOA formation and growth.

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